

Importance of High Angular-Momentum Channels in Pseudopotentials for Quantum Monte Carlo

William W. Tipton,¹ Neil D. Drummond,^{2,3} and Richard G. Hennig¹

¹*Department of Materials Science and Engineering,
Cornell University, Ithaca, New York 14853, U.S.A.*

²*Department of Physics, Lancaster University, Lancaster LA1 4YB, United Kingdom*

³*TCM Group, Cavendish Laboratory, University of Cambridge,
J. J. Thomson Avenue, Cambridge CB3 0HE, United Kingdom*

(Dated: May 15, 2014)

Quantum Monte Carlo methods provide in principle a highly accurate treatment of the many-body problem of the ground and excited states of condensed systems. In practice, however, uncontrolled errors such as those arising from the fixed-node and pseudopotential approximations can be problematic. We show that the accuracy of some quantum Monte Carlo calculations is limited by using available pseudopotentials. The use of pseudopotentials involves several approximations, and we will focus on one which is relatively simple to correct during the pseudopotential design phase. It is necessary to include angular momentum channels in the pseudopotential for excited angular momentum states and to choose the local channel appropriately to obtain accurate results. Variational and diffusion Monte Carlo calculations for Zn, O, and Si atoms and ions demonstrate these issues. Adding higher-angular momentum channels into the pseudopotential description reduces such errors without a significant increase in computational cost.

I. INTRODUCTION

Computational electronic structure methods have been extremely useful in developing our understanding of the atomic and electronic structures of real materials. As methods have become more accurate and their implementations increasingly efficient, simulations and calculations have taken some of the burden of finding and characterizing new materials off experimental work.¹

Density-functional theory (DFT), in particular, has been widely applied in recent decades. It is computationally efficient compared to other methods with similar accuracy, and robust, user-friendly software packages have made the method easy to apply. However, its accuracy is still insufficient for some applications, and the lack of a systematic way to improve its results or estimate its errors has hampered progress. In particular, electron correlation effects can be significant in many complex materials and are not captured accurately by many commonly-used density functionals. The development of functionals, which accurately describe the electronic band gap, van der Waals interactions, and other electronic properties of materials, is still an active area of research.²⁻⁵

These issues are overcome by methods which treat quantum many-body effects explicitly from the outset such as quantum Monte Carlo (QMC). QMC methods are among the most accurate many-body methods and can reliably and accurately predict ground-state expectation values for many systems. In fact, they have often been used as a benchmark for DFT work.⁶⁻⁹ Among the quantum Monte Carlo methods, variational Monte Carlo (VMC), diffusion Monte Carlo (DMC), and auxiliary-field quantum Monte Carlo¹⁰ are the most mature in terms of applicability to solid state systems. We treat only VMC and DMC in this work and refer to them col-

lectively as QMC.

As computers become faster and high-quality software packages for QMC such as CASINO,¹¹ QMCPACK,¹² QWALK,¹³ and CHAMP¹⁴ mature, these calculations are becoming less challenging. It is therefore important to identify and propagate the best-practice procedures for performing these calculations as they become more routine.

QMC and other correlated-electron methods usually employ the pseudopotential approximation to reduce the computational cost, particularly for heavy elements. The common form is the non-local, norm-conserving pseudopotential¹⁵ which applies different radial potential functions to each angular-momentum component of the wavefunction.

In this work, we determine the error in the energy due to an insufficient number of angular-momentum channels in the pseudopotential and discuss other sources of error in QMC calculations. We show that pseudopotentials that include channels to account for higher angular-momentum components of the wavefunction are necessary for performing accurate pseudopotential calculations in QMC. Such pseudopotentials are not the norm in the literature, and we suggest that this be corrected in order that QMC methods be suitable for routine application to scientifically and technologically interesting systems.

II. BACKGROUND

The computational cost of all-electron QMC scales approximately as $Z^{5.5}$ or $Z^{6.5}$ with respect to the atomic number.^{16,17} This makes the direct application of all-electron QMC to heavy atoms difficult. In practice, many properties of atoms are primarily due to the behavior of and interactions between valence electrons, and so a

pseudopotential approximation is commonly used to remove core electrons from the calculation and reduce the necessary computational effort.

Modern pseudopotentials are non-local in the sense that they act differently on distinct angular-momentum components of the wavefunction. This is necessary to accurately capture the effects of the nucleus and core electrons on the valence electrons, since the pseudopotential not only represents the effective electrostatic potential but also enforces orthogonality of valence orbitals to lower-energy states of the same angular momentum.

Of course, there is no clear distinction between core and valence electrons in many-body methods as the electrons are indistinguishable particles. Thus, the pseudopotential approximation does require neglecting exchange and correlation interactions between the valence and removed core electrons as well as that between the core electrons themselves. These errors are not explicitly accounted for in the calculations. However, the core-core interactions largely cancel out when considering energy differences, and the core-valence interactions may be kept small by a choice of core size which leads to significant spatial separation between the core and valence electron densities. These techniques may be able to produce results as accurate as all-electron calculations.¹⁷ Additionally, the use of core-polarization potentials can account for some core-valence correlations.^{18–20}

To introduce non-local pseudopotentials in QMC, the electron-ion potential of any given atom is divided into a local potential, \hat{V}_{loc} , and a nonlocal potential operator, \hat{V}_{nl} . The local potential is applied to the whole wavefunction, and the nonlocal corrections account for the differences between the local potential and the potentials that should be seen by each angular-momentum component of the wavefunction:

$$\hat{V}_{\text{loc}} + \hat{V}_{\text{nl}} = \sum_{i=1}^{N_{\text{el}}} V_{\text{loc}}^{\text{ps}}(r_i) + \sum_{i=1}^{N_{\text{el}}} \hat{V}_{\text{nl},i}^{\text{ps}}. \quad (1)$$

The nonlocal potential operator $\hat{V}_{\text{nl},i}^{\text{ps}}$ acts on a function $f(\mathbf{r}_i)$ by

$$\hat{V}_{\text{nl},i}^{\text{ps}} f(\mathbf{r}_i) = \sum_{l,m} V_{\text{nl},l}^{\text{ps}}(r_i) Y_{lm}(\Omega_i) \int_{4\pi} Y_{lm}^*(\Omega'_i) f(\mathbf{r}'_i) d\Omega'_i, \quad (2)$$

where the angular integral in the operator projects the wavefunction onto spherical harmonics. The $V_{\text{nl},l}^{\text{ps}}(r)$ are functions of only the electron-nuclear distance r and account for the difference between the desired l -dependent potential and the local channel. The local potential, or local channel, $V_{\text{loc}}^{\text{ps}}(r)$, is by convention chosen to be the exact potential associated with one of the angular-momentum components, so the sum in Eq. (2) need not include this local component.⁶

The choice of local channel itself is arbitrary but is often chosen for convenience during the pseudopotential design process. In particular, judicious choice of the local channel is often necessary to avoid the problem of ghost

states which can arise due to the Kleinman-Bylander transformation.²¹ The same choice of local channel that is suitable for that transformation may not be optimal with regards to accuracy of QMC calculations.²²

In an independent electron theory such as Hartree-Fock or DFT, atomic wavefunctions are composed of some number of the lowest-energy single-particle orbitals. For example, in these frameworks, the electronic configuration of an oxygen atom may be written as $1s^2 2s^2 2p^4$. Notice that this wavefunction contains no angular-momentum components above $l = 1$. Thus, a non-local pseudopotential in the above form which acts on these single-atom wavefunctions need not include terms $V_{\text{nl},l}^{\text{ps}}$ for $l > 1$ if it is to be used to calculate ground-state atomic properties using a one-electron theory.

The situation is not so simple in the case of solids and other extended systems where bonding changes the wavefunctions in a way that effectively introduces higher angular-momentum components. Indeed, in the case of systems such as bulk Si and other second row elements, wavefunctions with higher angular-momentum character will be present. In this case, it may be necessary to use a pseudopotential with a d -channel, even at the DFT level (especially in the high-pressure regime). However, these errors often cancel when considering energy differences and are frequently neglected in practice.^{23,24}

In QMC and other correlated-electron methods, excitations of the wavefunction into higher angular-momentum states arise immediately, *i.e.*, even for isolated atoms. In VMC, wavefunctions may be represented by the product of a Slater determinant of single particle orbitals and the so-called Jastrow factor. The Jastrow is a positive function of inter-particle distances, and its purpose is to directly account for many-body correlation effects. Naturally, the VMC wavefunction is then no longer entirely composed of the lowest-order spherical harmonics. The situation in DMC and other correlated-electron methods is analogous.⁶

Notice from Eq. (1) that, in the absence of a pseudopotential channel to deal with the higher-angular momentum components of the wavefunction, these components simply feel the local channel. This is incorrect and may be drastically so, especially in the case where the local channel was designed to enforce orthogonality to the lower-energy orbitals with a particular angular momentum. This can lead to sizable errors in total energy calculations.

Now, this effect is not a particularly surprising one and certainly has been understood by some in the density-functional theory community since the beginnings of the use of pseudopotentials in that field (see, for example, Ref. 25). However, inclusion of so-called higher angular-momentum channels is not the normal practice in the development of potentials for use with QMC.

There are a limited number of pseudopotential types available for use with QMC. The application of projector-augmented waves²⁶ or ultra-soft pseudopotential²⁷ tech-

TABLE I. Choices of angular-momentum channels and local channels for the various pseudopotentials considered for oxygen, silicon and zinc.

	Standard		Augmented	
	Channels	Local	Channels	Local
O	s, p	s or p	s, p, d	s or p
Si	s, p	s or p	s, p, d	s or p
Zn	s, p, d	s or d	s, p, d, f	s, d , or f

niques in QMC is currently not feasible since the DMC operators for the projectors and the augmentation charge are unknown, but a number of semi-local pseudopotentials have been developed with QMC applications in mind. Greeff *et al.* developed a carbon pseudopotential which included s - and p -channels.²⁸ Ovcharenko *et al.* applied a similar methodology to produce pseudopotentials for Be to Ne and Al to Ar with $l_{\max} = 1$.²⁹ Burkatzki *et al.* present potentials for many of the main group elements³⁰ and for the $3d$ transition metals.³¹ Their Si and Zn potentials have 3 channels, and their O potential has 2. These authors all cite the rule of thumb that l_{\max} should be at least as high as the highest angular-momentum component in the atomic core. Trail *et al.* developed a variety of pseudopotentials for all elements from H to Hg. These all have exactly 3 channels and are associated with the CASINO code which, until recently, only supported pseudopotentials with exactly 3 channels.³²

III. METHODOLOGY

We determine how the number of channels and the choice of local channel affects the energy for several atoms and ions. We compute the total energies and first and second ionization energies of the oxygen, silicon, and zinc atoms using several related pseudopotentials. These elements provide interesting test cases due to their varied electronic structures. Additionally, we are interested in the application of QMC methods to bulk semiconductors such as Si and ZnO.^{8,9}

Hartree-Fock (HF) pseudopotentials were generated with the OPIUM code³³ using the Troullier-Martins (TM)³⁴ and Rappe-Rabe-Kaxiras-Joannopoulos (RRKJ)³⁵ methods. HF has been found to be preferable to DFT for the generation of pseudopotentials for many-body methods.²⁸ A singly ionized reference configuration was used, and a grid search over the design parameter space (including fitting method) was performed with the objective of minimizing error under the fitting theory for pseudopotential and all-electron valence energy levels for a set of test configurations. Some preference was given to softness of the potentials as well. In case that parameters corresponding to high angular momentum channels had no effect on the energies at the single particle level of theory, parameters were chosen identical to the next-

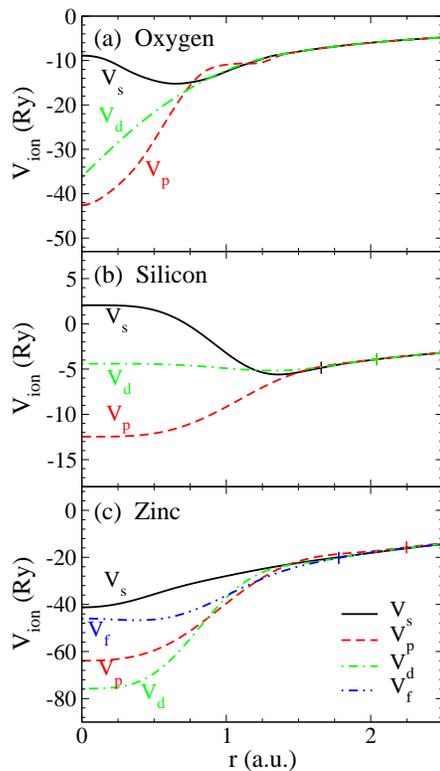


FIG. 1. (color online) Pseudopotentials for O, Si, and Zn.

highest channel. In the end, we used an RRKJ pseudopotential for oxygen and TM pseudopotentials for zinc and silicon. Mean absolute errors at the HF level were 7 meV, 10 meV, and 33 meV for the O, Si, and Zn fits, respectively.³⁶

Table I lists the angular-momentum channels and the choice of local channel for each pseudopotential. For each element, we consider (i) pseudopotentials with the minimum number of channels (s and p for O and Si; s, p and d for Zn) and (ii) pseudopotentials that contain an additional angular-momentum channel (d for O and Si; f for Zn). We refer to the first set as *standard* pseudopotentials and the second as *augmented*. For the local channel, we consider the s and p channels for O and Si and the s, d or f channels for Zn. One (augmented) pseudopotential was fit for each element, and then appropriate channels removed to obtain the standard versions. The choice of local channel can be delayed until the energy calculation. This results in the 13 pseudopotentials listed in Table I.

Figure 1 shows the distance dependence of the angular momentum channels for the various pseudopotentials. For Si and Zn, we confirmed that the pseudopotentials accurately describe the lattice parameters of the ground state crystal structure and for O, we confirmed that the pseudopotential reproduces the dimer bond length at the DFT level.

QMC calculations were performed using the CASINO code.¹¹ We implemented support for pseudopotentials with an arbitrary number of angular-momentum chan-

nels in CASINO. Total energy calculations are performed on the 9 isolated ions with each of the applicable pseudopotentials. Our Slater-Jastrow trial wavefunctions consisted of a Jastrow factor multiplying a linear combination of Slater determinants of single-particle orbitals. The minimum number of Slater determinants was chosen to account for the correct spin groundstates of the atoms and ions; a single determinant was sufficient for the case of O^+ , Si^{2+} , Zn^0 , Zn^+ , and Zn^{2+} , while three determinants were required for O^0 , O^{2+} , Si^0 , and Si^+ . The single-particle orbitals were generated using the PWSCF code³⁷ with the B3LYP exchange-correlation functional³⁸ and for efficiency were expressed in a B-spline basis.^{39,40} Plane-wave cutoffs of 70 Ry for oxygen and silicon and 100 Ry for zinc were used to converge the total energies to 2 meV. Occupancies were fixed so that the wavefunctions have the correct symmetry.

The Jastrow factor is a non-negative function of inter-particle distances and includes two-body electron-electron and electron-nucleus and three-body electron-electron-nucleus terms as implemented in CASINO.⁴¹ Parameters were added to the Jastrow factor of the trial wavefunction gradually during its optimization. The Jastrow parameters were optimized using variance minimization⁴² followed by energy minimization in the final step.⁴³ The backflow transformation⁴⁴ was not found to provide any significant benefit in these cases. Trial wavefunctions were evaluated by their mean energy plus three times the statistical error in the energy, following Ref. 45.

Several additional details of our VMC calculations are noteworthy. First, the integral in Equation (2) is performed on a spherical grid in real space. This integration mesh must be chosen to be sufficiently dense to accurately calculate the contributions to the energy from higher angular-momentum components of the wavefunction and thus evaluating the effects which are the focus of this paper. Secondly, it is the default behavior of the CASINO code that the non-local contributions to the energy are assumed constant and are not recalculated during a variance minimization step. In many systems, this improves the runtime of the algorithm significantly while still giving good results — in some cases it actually improves the performance of the variance minimization. However, as we will see, the non-local contributions are significant in many of our calculations. We found it necessary in many cases to recalculate the non-local contributions to the energy at each step of the optimization to ensure the stability of the optimization process during Jastrow optimization.

Our DMC calculations were performed using the pseudopotential locality approximation.⁴⁶ For each system, we performed at least $256 \cdot 10^6$ steps with a target population of 2,000 walkers. We carried out the DMC calculations using a time steps of 0.0025 and 0.01 Ha^{-1} and extrapolated the DMC results to a zero time step, obtaining corrections to the total energies of less than 1, 9, and 25 meV in the total energies and 1, 6, and 6 meV in the ionization energies for Si, O, and Zn, respectively.

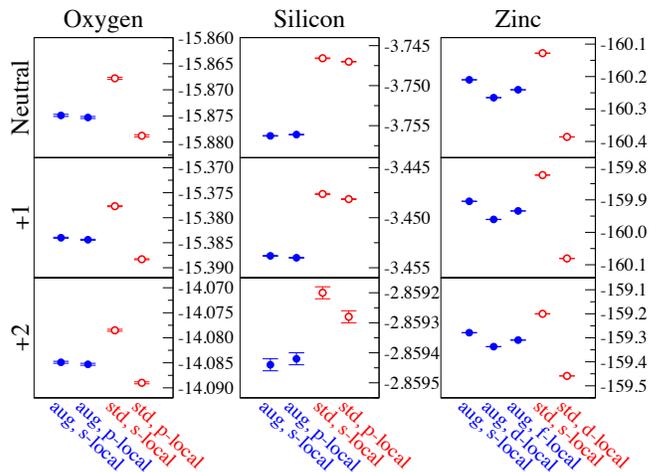


FIG. 2. (color online) Total VMC energy in Hartree and statistical error in the energy of each species with respect to each Hamiltonian. Pseudopotentials are denoted according to the choice of local channel and ‘aug’ if they are augmented with an additional channel or ‘std’ otherwise.

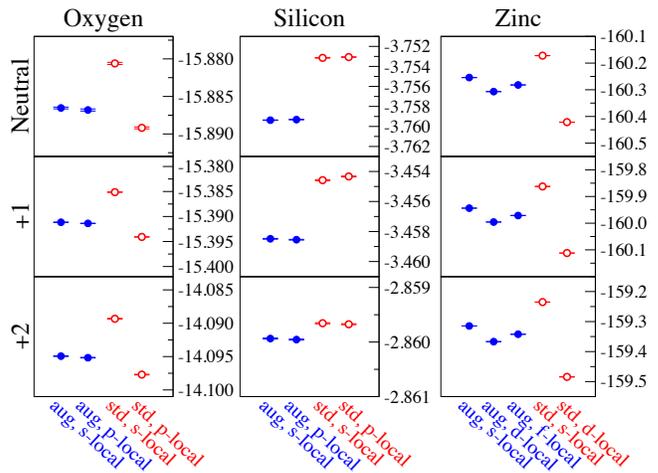


FIG. 3. (color online) Total DMC energy in Hartree and statistical error in the energy of each species with respect to each Hamiltonian. Pseudopotentials are labeled as in Fig. 2.

Finally, atomic ionization energies are simply differences between the total energies of the appropriate species.

IV. RESULTS AND DISCUSSION

Figures 2 and 3 show the energies for each ion-pseudopotential combination for VMC and DMC, respectively. The error bars indicate only the statistical uncertainties in the energies associated with the QMC calculations. First, it is important to notice the scale of the axes. The magnitude of variation in the total energies differs between the three elements; for Si, it is on the order of milli-Hartrees, while for Zn, it is on the order of tenths of Hartrees, with oxygen falling in between.

the augmented potentials and the highest angular momentum channel as the local channel. This close agreement indicates not only the accuracy and usefulness of the optimized pseudopotentials for O and Si but also that the neglect of core-polarization and relaxations as well as core-valence correlations for these atoms has a small effect on the ionization energies.

For the case of Zn, we observe significantly larger errors of about 1 eV for the 1st and 2nd ionization energy. Several sources of errors may explain the deviation of our pseudopotential results from experimental values. We calculated spin-orbit corrections to the total energies at the DFT level and found that they largely cancel in the ionization energies, resulting in corrections too small to account for the observed differences in the ionization energies between QMC and experiment (less than 3 meV for O and less than 1 meV for Zn).

The pseudopotential approximation itself leads to several errors other than those focused on in this paper. By removing explicit treatment of core electrons from the calculation, we neglect correlations between the core and valence electrons. This is minimized but not altogether eliminated by designing pseudopotentials so that the core and valence electrons are spatially separated. The core-valence correlation may be particularly important for the case of zinc where the $3d$ valence electron states have sizable spatial overlap with the $3p$ core electron states and may explain the large errors in the ionization energies there. However, the magnitude of corrections obtained using published core-polarization potentials³² was negligible.

Pseudopotential calculations for Sc and Ti using small-core pseudopotentials by Burkatzki *et al.* resulted in DMC ionization energies up to 0.4 eV above the experimental value, indicating that including the $3p$ states in the valence somewhat improves the accuracy. However, calculations of the ionization energies for the same pseudopotential using CCSD(T), a many-body quantum chemistry method, resulted in significantly improved ionization energies compared to DMC, indicating that it is not the pseudopotential approximation but the fixed-node approximation that may be the dominant source of errors in their case.³¹

Evaluation of the pseudopotentials in DMC is subject to the locality approximation⁴⁶ used in this work or the lattice-regularized method by Casula.⁵³ Pozzo and Alfe⁵⁴ found that, in magnesium and magnesium hydride, the errors of the locality approximation and the lattice-regularized method are comparably small, but that the lattice-regularized method requires a much smaller DMC time step. We calculated oxygen ionization energies using the lattice-regularized method of Casula and found the results changed by less than 30 meV.

In addition to the pseudopotential approximation, a second primary source of errors in our O and Zn ionization energies at the DMC level arises from the fixed-node approximation. Fixed node errors can be eliminated by providing an initial trial wavefunction with correct nodal

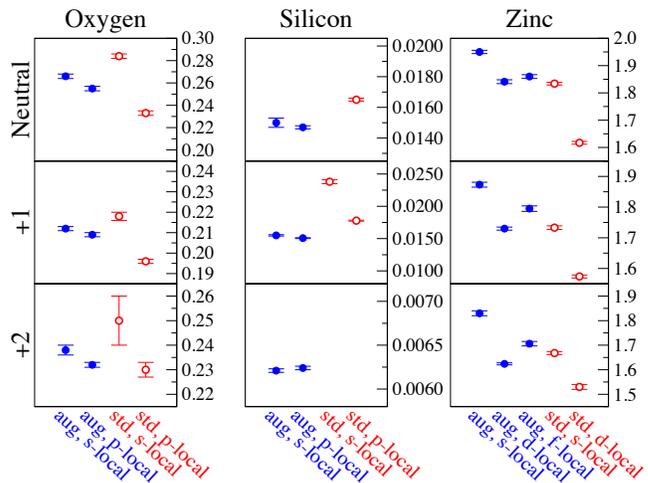


FIG. 5. (color online) Variance in local energy in atomic units and associated statistical error of each VMC calculation. Hamiltonians are labeled as in Figure 2.

structure. Variances in the local energy for each VMC calculation are shown in Fig. 5. Eigenstates of the Hamiltonian have zero variance, and higher variances typically indicate a worse approximation of the ground-state wavefunction. High variances can originate from poor single-particle orbitals or from difficulty optimizing the parameters of the Slater-Jastrow trial wavefunctions and are indicative of poorly-optimized variational wavefunctions.

Figure 5 indicates that our optimized trial wavefunctions are best for Si and increasingly worse for O and Zn. For silicon, our variational Slater-Jastrow were well-optimized as evidenced by the low variance in the local energy. The fixed node error is correspondingly small, and we see that the choice of local channel and inclusion of higher angular momentum channels has a clear bearing on the accuracy of calculated ionization energies. In the case of oxygen and zinc, the effect of these pseudopotential design choices on our results was swamped by other issues which made it difficult to obtain good trial wavefunctions at the VMC level.

A possible reason for the trouble in optimizing a Slater-Jastrow wavefunction for Zn stems from the poor description of the $3d$ -levels of the zinc atom in DFT. Semilocal functionals are known to place the $3d$ level of the Zn atom significantly too high.^{55,56} This results in an incorrect description of the d -channel of the pseudopotential and of the $3d$ -orbital in the trial wave function which is reflected in both the large energy variance and large deviation of the QMC ionization energy from experiment. Each of these issues could lead to suboptimal VMC trial wavefunctions and then, by way of the fixed-node approximation, to errors in the DMC results.

V. CONCLUSIONS

In this paper, we have shown that pseudopotentials which include channels to account for higher angular-momentum components of the wavefunction are necessary for performing accurate pseudopotential calculations in QMC. For O, Si and Zn, we determined how the number of angular-momentum channels and the choice of local channel in the pseudopotential affects the total energy and ionization energies of these atoms in QMC. We find a sizable error in the total energies for any choice of local channel when the pseudopotentials do not include at least one additional angular-momentum channel above the highest angular-momentum component of the ground state wavefunction of the atom. This is because, contrary to single-electron mean-field methods such as DFT and HF, atomic ground state wavefunctions in correlated-electron methods include higher angular-momentum character. These components effectively see the wrong potentials when using standard pseudopotentials.

This effect was demonstrated for the case of isolated ions where it is least severe. Because of the effect of bonding on the wavefunctions, this situation is expected to be more pronounced in the case of solids and molecules. Nonetheless it appears to be the dominant source of error in our calculated silicon ionization energies. In the case of zinc and oxygen, it has an effect of similar magnitude, but errors arising from the pseudopotential and fixed node approximations appear to dominate at the DMC level.

All-electron, single-determinant QMC methods ob-

tain very high accuracy and are systematically improvable through the use of multi-determinant wavefunctions. However, the pseudopotential approximation is often a practical necessity. Although QMC methods are becoming more widely used, they are still not routine, and best practices for obtaining reliable results are still evolving. Our results suggest that one such best practice is to include at least one channel in the pseudopotential above the highest angular-momentum component of the ground state wavefunction in single-particle methods. Additionally, this highest channel should be used as the local channel as it will generally be most similar to missing, yet-higher angular-momentum channels.

VI. ACKNOWLEDGMENTS

The authors would like to thank John Trail and Richard Needs for helpful discussions. This research has been supported by the Cornell Center for Materials Research NSF-IGERT: A Graduate Traineeship in Materials for a Sustainable Future (DGE-0903653), by the National Science Foundation under Award Number CAREER DMR-1056587, and by the Energy Materials Center at Cornell (EMC2), funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001086. This research used computational resources of the Texas Advanced Computing Center under Contract Number TG-DMR050028N and of the Computation Center for Nanotechnology Innovation at Rensselaer Polytechnic Institute.

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